AD-A150 301 SEQUENTIAL EXCITATION PREPARATION OF MOLECULAR ENERGY LEVELS WITH SPECIAL.. (U) MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF CHEMISTRY R W FIELD ET AL. 26 NOV 84 1/1

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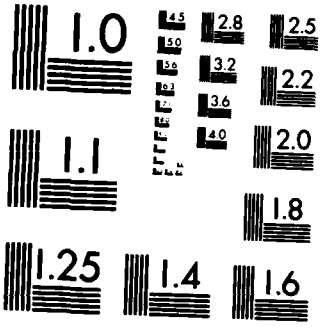

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DOCUMENTATION PAGE

1a. REI Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR- 84-1251
6a. NAME OF PERFORMING ORGANIZATION Massachusetts Institute of Technology (6b. OFFICE SYMBOL (If applicable))	7a. NAME OF MONITORING ORGANIZATION AFOSR/NC
6c. ADDRESS (City, State and ZIP Code) Department of Chemistry Massachusetts Institute of Technology Cambridge, MA 02139	7b. ADDRESS (City, State and ZIP Code) Bldg. 410 Bolling Air Force Base Washington, D.C. 20332-6448
8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR (8b. OFFICE SYMBOL (If applicable) NC)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F49620-83-C-0010
8c. ADDRESS (City, State and ZIP Code) AFOSR/NC Bldg. 410 Bolling Air Force Base Washington, D.C. 20332-6448	10. SOURCE OF FUNDING NOS. PROGRAM ELEMENT NO. 61102F; PROJECT NO. 2303; TASK NO. B1; WORK UNIT NO. A

11. TITLE (Include Security Classification) Sequential Excitation Preparation of Molecular Energy Levels with Special Structural and Chemical Properties (Unclassified)

12. PERSONAL AUTHOR(S) Robert W. Field and James L. Kinsey

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Yr., Mo., Day)	15. PAGE COUNT
Final	FROM 1 Oct 83 TO 30-9-84	26 November 1984	10

16. SUPPLEMENTARY NOTATION This report Pertains to: Contid

17. COSATI CODES		
FIELD	GROUP	SUB. GR.

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Spectroscopy, Vibrational Structure, Optical-Optical Double Resonance, Molecular Dynamics, Anharmonic Vibrational Constants, Electric Dipole Moment, Coriolis Perturbations, Quantum Chaos, Keywords Cont'd

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A. Stimulated Emission Pumping Studies of Formaldehyde.

The Stimulated Emission Pumping (SEP) technique was applied for the first time to a polyatomic molecule, H_2CO. SEP spectroscopy has provided an unprecedentedly complete picture of the structure of H_2CO at high levels of excitation. A complete set of anharmonic vibrational constants, ω_i and x_{ij}, was obtained from data on more than 80 vibrational levels at energies up to 9300 cm^{-1}. Nonrotating H_2CO is vibrationally well organized at $E \leq 9300 cm^{-1}$, but rotation causes significant mode mixing. This implies that structurally quite distinct nonrotating levels coexist with structurally indistinguishable rotating levels and that level-specific chemistry, if it will ever be observable, must compete with rotational thermalization. Measures of quantum ergodicity were applied to the H_2CO SEP spectra with the surprising result that, even though the spectra sample more levels as the rotational quantum numbers J and K are increased, a decreasing fraction of accessible phase space is sampled.

B. The $H_2CO(S_0) \rightarrow H_2+CO$ Barrier. Stark Quantum Beat and $S_0 \sim S_1$ Anticrossing Spectroscopy were

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☒ DTIC USERS ☐	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE NUMBER (Include Area Code)	22c. OFFICE SYMBOL
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DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE. Unclassified SECURITY CLASSIFICATION OF THIS PAGE

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18. (Keywords continued):
Anticrossing and Quantum Beat Spectroscopy, Barrier to Dissociation, Rotational Energy Transfer, Formaldehyde.

1A sub 1 Level

19. (Abstract continued):
used to measure the homogeneous width of two S_0 rotation-vibration levels near the top of the S_0 barrier. A result at variance with simple RRKM theory was obtained: for two J=2 levels separated by 31 cm^{-1}, the higher energy level penetrates the barrier a factor of 2.5 slower than the lower energy level. An upper bound to the S_0 barrier is obtained.

C. Collisional Studies of H_2CO $\tilde{A}\ ^1A_1$.
Two pulsed-cw variants of SEP, Transient Gain and Transient Polarization Spectroscopy enable measurement of single-J level collisional depopulation and depolarization rates and state-to-state transfer rates free of the multiple-collision effects and limited resolution of resolved fluorescence studies.

2S level 2P level

D. Spectroscopic Studies of Na_2
Two new techniques were demonstrated. Modulated gain spectroscopy has allowed observation of the levels of ~~the~~ Na_2 $A\ ^1\Sigma_u^+$ and $B\ ^1\Pi_u$ states near the $Na(^2S)+Na(^2P)$ dissociation limit. Perturbation facilitated Optical-Optical Double Resonance has made the Na_2 triplet valence and Rydberg states accessible to sub-Doppler spectroscopy.

Originator furnished Keywords include:

See Below

FINAL REPORT

SEQUENTIAL EXCITATION PREPARATION OF MOLECULAR ENERGY LEVELS WITH SPECIAL STRUCTURAL AND CHEMICAL PROPERTIES

ROBERT W. FIELD AND JAMES L. KINSEY

F49620-83-C-0010

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MA 02139

1 October 1982 - 30 September 1984

B. Research Objectives

1. Apply the Stimulated Emission Pumping (SEP) technique to highly excited vibrational levels of a polyatomic molecule.
2. Discover whether the rotation-vibration states of a polyatomic molecule remain well organized at chemically significant levels of vibrational excitation.
3. Develop new multiple-resonance spectroscopic techniques.
4. Examine the near-dissociation levels of the I_2 and Na_2 molecules.
5. Develop spectroscopic diagnostics for the metastable states of the alkaline earth monoxides.

C. Status of Research Effort

All of the cited objectives have been achieved. Research in areas 1-3 is continuing under a new AFOSR contract and in area 4 under an NSF grant.

1. H_2CO was the first polyatomic molecule studied by SEP. An unprecedentedly complete set of anharmonic vibrational constants and electric dipole moments was obtained by SEP and SEP-Stark spectroscopy. More than 50 vibrational levels of the $\tilde{X}\ ^1A_1$ state were observed and assigned. SEP has been proven to be a high resolution spectroscopic technique well suited to the study of polyatomic molecular rotation-vibration structure in energy regions where the density of states had previously prohibited systematic study of fully resolved and assigned spectra.

2. The vibrational levels of $H_2CO\ \tilde{X}\ ^1A_1$ at energies up to 9300 cm^{-1} were found to be surprisingly well organized in the absence of rotation yet almost completely disorganized for $J = 10$, $K_a = 2$. Coriolis coupling appears

to destroy the usual normal/local mode vibrational quantum numbers and to destroy partially the K_a, K_c rotational indices as well. Statistical measures of quantum ergodicity were applied to the H_2CO SEP spectra.

3. Stark AntiCrossing (SAC) and Stark Quantum Beat (SQB) spectroscopy was used for the first time on a polyatomic molecule to determine the tunnelling lifetimes of two highly excited levels of S_0 H_2CO through the barrier to dissociation into H_2 + CO. The observed tunnelling rates are not in accord with the usual interpretation of RRKM reaction rate theory; the higher (by 31 cm^{-1}) of two levels with the same J and rotation-vibration symmetry tunnels a factor of 2.5 more slowly.

Modulated Gain Spectroscopy (MGS) was applied to the near dissociation levels of the Na_2 $A^1\Sigma_u^+$ and $B^1\Pi_u$ states. All of the vibrational levels of $B^1\Pi_u$ quasi-bound behind the intrinsic potential barrier were observed and tunnelling rates thorugh the barrier to Na(3S) + Na(3P) were measured.

Perturbation-Facilitated Optical-Optical Double Resonance (PFOODR) spectra of triplet states of Li_2 and Na_2 were observed by taking advantage of spin-orbit $A^1\Sigma_u^+$-$b^3\Pi_u$ perturbations. The first rotationally resolved and assigned spectra of $^3\Lambda_g$ Rydberg states and the $a^3\Sigma_u^+$ and $b^3\Pi_u$ valence states of Li_2 and Na_2 were recorded.

4. Analysis was completed of the long range behavior and mutual perturbations of the I_2 $X^1\Sigma_g^+$, $a'0_g^+$, and $a1_g$ states near the $I(^2P_{3/2})$ + $I(^2P_{3/2})$ dissociation asymptote. High quality, sub-Doppler spectra were obtained (in Orsay, France) by Laser Induced Fluorescence-Fourier Transform Spectroscopy (LIF-FTS). A separated atom formalism accounts for all electronic properties of all 36 I_2 electronic states at the lowest three dissociation asymptotes.

MGS spectra of the Na_2 $A^1\Sigma_u^+$ and $B^1\Pi_u$ states provided accurate long range constants for all states of Na_2 arising from the Na(3S) + Na(3P) limit. Accurate values for the Na(3P←3S) oscillator strength and the Na(3P) dipole polarizability tensor atomic properties were determined from molecular energy levels.

PFOODR spectra of the Na_2 $a^3\Sigma_u^+$ state provided the first characterization of this mostly repulsive lowest triplet state which has significant population in an Na_2 heat pipe. A combined analysis of the Na_2 $X^1\Sigma_g^+$ and $a^3\Sigma_u^+$ states provides an accurate measure of the exchange interaction between Na(3S) atoms.

5. The CaO $D,d^1,^3\Delta$-$a^3\Pi$ and $c^3\Sigma^+$-$a^3\Pi$ systems were examined at sub-Doppler resolution, rotationally analyzed, and deperturbed. Accurate frequencies and linestrength factors are now available for J,Ω,e/f state-specific monitoring of population in the CaO metastable $a^3\Pi$ and $A'^1\Pi$ states.

D. List of Publications

"Rotation-Vibration Analysis of BO_u^+-al_g and BO_u^+-$a'O_g^+$ Electronic Systems of I_2 by Laser-Induced-Fluorescence Fourier-Transform Spectroscopy", S. Churassy, F. Martin, R. Bacis, J. Verges, and R. Field, J. Chem. Phys. 75, 4863-4868 (1981).

"Tunable Laser Electronic Spectroscopy", R.W. Field, Disc. Faraday Soc. 71, 111-123 (1981).

"Assignments of the N_2 $W^3\Delta$-$B^3\Pi$ and $B^3\Pi$-$W^3\Delta$ Lasing Lines", D. Cerny, R. Bacis, R.W. Field, and R.A. McFarlane, J. Phys. Chem. 85, 2626-2631 (1981).

"Selective Vibrational Excitation by Stimulated Emission Pumping", C. Kittrell, E. Abramson, J.L. Kinsey, S. McDonald, D.E. Reisner, D. Katayama, and R.W. Field, J. Chem. Phys. 75, 2056-2059 (1981).

"Highly Excited, Normally Inaccessible Vibrational Levels by Sub-Doppler Modulated Gain Spectroscopy: The Na_2 $A^1\Sigma_u^+$ State", H.S. Schweda, G.K. Chawla, and R.W. Field, Opt. Commun. 42, 165-170 (1982).

List of Publications (continued):

"The CaO D,d^1,$^3\Delta$-$a^3\Pi$ System: Sub-Doppler Spectrum, Rotational Analysis, and Deperturbation", R.F. Marks, R.A. Gottscho, and R.W. Field, Physica Scripta 25, 312-328 (1982).

"The Orange Arc Bands of CaO: Analysis of a D,d^1,$^3\Delta$-$a^3\Pi$ System", R.F. Marks, H.S. Schweda, R.A. Gottscho, and R.W. Field, J. Chem. Phys. 76, 4689-4691 (1982).

"Selective Vibrational Excitation of Formaldehyde $\tilde{X}^1A_1$ by Stimulated Emission Pumping", D.E. Reisner, P.H. Vaccaro, C. Kittrell, R.W. Field, J.L. Kinsey and H.-L. Dai, J. Chem. Phys. 77, 573-575 (1982).

"Laser Population of Highly Excited Vibrational Levels of Molecules", E. Abramson, H.-L. Dai, R.W. Field, D.G. Imre, J.L. Kinsey, C. Kittrell, D.E. Reisner, and P.H. Vaccaro, in Lasers as Reactants and Probes in Chemistry, W. Jackson (ed.), Howard University, 1982.

"Electric Dipole Moments of Excited Vibrational Levels in the $\tilde{X}^1A_1$ State of Formaldehyde by Stimulated Emission Spectroscopy", P.H. Vaccaro, J.L. Kinsey, R.W. Field, and H.-L. Dai, J. Chem. Phys. 78, 3659-3664 (1983).

"Long Range Behavior of the Gerade States Close to the $^2P_{3/2} + {}^2P_{3/2}$ Iodine Dissociation Limit by Laser-Induced Fluorescence Fourier-Transform Spectroscopy", F. Martin, S. Churassy, R. Bacis, R.W. Field, and J. Verges, J. Chem. Phys. 79, 3725-3737 (1983).

"Direct Observation of High-Lying $^3\Pi_g$ States of the Na_2 Molecule by Optical-Optical Double Resonance," Li Li and R.W. Field, J. Phys. Chem. 87, 3020-3022 (1983).

"Stimulated Emission Spectroscopy: A Complete Set of Vibrational Constants for $\tilde{X}\ ^1A_1$ Formaldehyde", D.E. Reisner, R.W. Field, J.L. Kinsey, and H.-L. Dai, J. Chem. Phys. 80, 5968-5978 (1984).

"Rotation Induced Vibrational Mixing in $\tilde{X}\ ^1A_1$ Formaldehyde: Nonnegligible Dynamical Consequences of Rotation", H.-L. Dai, C.L. Korpa, J.L. Kinsey, and R.W. Field, J. Chem. Phys. 00, 0000-0000 (1984).

State-Specific Rates of $H_2CO(S_0) \rightarrow H_2 + CO$ at Energies Near the Top of the Barrier: A Violation of RRKM Theory?", H.-L. Dai, R.W. Field, and J.L. Kinsey, J. Chem. Phys. 00, 0000-0000 (1985).

"Intramolecular Vibrational Dynamics Including Rotational Degrees of Freedom: Chaos and Quantum Spectra", H.-L. Dai, R.W. Field, and J.L. Kinsey, J. Chem. Phys. 00, 0000-0000 (1985).

E. Personnel

1. Visiting Scientists

Prof. Roger Bacis (I_2 LIF-FTS)
Universite Claude Bernard
Villeurbanne, France

Dr. Serge Churassy (Na_2 MGS)
Universite Claude Bernard
Villeurbanne, France

Prof. K.K. Innes (H_2CO SEP)
State University of New York
Binghamton, New York

Dr. Daniel Katayama (H_2CO SEP)
Air Force Geophysics Laboratory
Hanscom Air Force Base
Bedford, Massachusetts

Prof. Richard Redington (H_2CO SEP)
Texas Tech University
Lubbock, Texas

Prof. Jan Schmidt (H_2CO Coherent Raman Beats)
Huygens Laboratorium
University of Leiden
Leiden, The Netherlands

2. Postdoctoral Associates

Dr. Hai-Lung Dai*	(H_2CO SEP, SQB, SAC)
Dr. Carter Kittrell	(H_2CO SEP)
Dr. Li Li	(Na_2 PFOODR)
Dr. Hartmut Schweda	(Na_2 MGS, CaO)
Dr. Joachim Vedder	(Na_2 MGS)
Dr. Xingbin Xie	(Li_2 PFOODR)

3. Graduate Students

Ms. Gunjit Chawla* (Na_2 MGS)
Ph.D. January 1985

Mr. Caba Korpa* (H_2CO SEP, Coriolis)

Mr. Ronald Marks ($CaO\ D,d^1,^3\Delta\text{-}a^3\Pi$)
S.M. February 1981

Graduate Students (continued):

Dr. Stephen McDonald (SEP)
Ph.D. December 1984

Mr. Jeffrey Norman ($CaO\ c^3\Sigma^+ - a^3\Pi$)

Dr. David Reisner* (H_2CO SEP)
Ph.D. September 1983

Mr. Patrick Vaccaro* (H_2CO SEP, SQB)

4. *Undergraduates*

Mr. Martin Carrera
B.S. May 1983

Ms. Ann Zabludoff

F. Interactions: Spoken Papers

1. R.W. Field, "Stimulated Emission Pumping," 181st Meeting of American Chemical Society, Atlanta (Nobel Laureate Signature Award Session), Talk 61.

2. J.L. Kinsey, "Laser Photons as Analytic and Synthetic Reagents in Studies of Reaction Dynamics," 181st Meeting of American Chemical Society, Atlanta (Peter Debye Award Symposium), Talk 19.

3. J.L. Kinsey, "Laser Population of Highly Excited Vibrational Levels of Molecules," Conference on Lasers as Reactants and Probes in Chemistry, Howard University (May 1982).

4. J.L. Kinsey, "An Outsider's View of the Spectroscopy of Polyatomic Systems - Bound and Continuum States," Distinguished Speakers Series, Department of Chemistry, University of Utah (May 1982).

5. J.L. Kinsey, "Stimulated Emission Pumping: An Easy Route to Highly Excited Levels of Polyatomic Molecules," Aerodyne Corp. (January 1982).

6. J.L. Kinsey, same as #5, Brown University, Department of Chemistry (January 1982).

7. J.L. Kinsey, "Study of Vibrationally Hot Molecules by Stimulated Emission," Yale University, Department of Chemistry (February 1982).

8. R.W. Field, "Vibrationally Very Hot Molecules," Laboratoire de Photophysique Moléculaire," Orsay, France (December 1981).

9. R.W. Field, "Do Highly Excited Molecules Have a Structure?" Symposium on Lasers in Spectroscopy and Technology, M.I.T. (May 1982).

10. R.W. Field, "Vibrationally Excited Formaldehyde and Acetylene," Informal Conference on Photochemistry, SRI International (June 1982).

11. R.W. Field, "Stimulated Emission Pumping," Freie Universität Berlin (March 1982).

12. R.W. Field, same as #11, Aerodyne (June 1982).

13. R.W. Field, "Stimulated Emission Pumping: Vibrational Energy Redistribution in H_2CO and HCCH?" Harvard University, Department of Chemistry (February 1983).

14. R.W. Field, same as #13, Notre Dame Radiation Laboratory (March 1983).

15. R.W. Field, same as #13, University of Colorado, Joint Institute of Laboratory Astrophysics (May 1983).

16. R.W. Field, same as #13, Denver University, Department of Chemistry (May 1983).

Interactions: Spoken Papers (continued):

17. R.W. Field, "Vibrationally Hot Molecules: A Search for a Needle in a Haystack," University of Pittsburgh, Department of Chemistry (November 1982).

18. R.W. Field, "Stimulated Emission Pumping," Lasers 82, New Orleans (December 1982).

19. R.W. Field, same as #18, North East Regional Meeting of the American Chemical Society, Hartford (June 1983).

20. H.-L. Dai, P.H. Vaccaro, E. Abramson, M. Lombardi, K.K. Innes, R.W. Field, and J.L. Kinsey, "Vibrational Energy Redistribution in H_2CO and HCCH? Quantum Beat and Stimulated Emission Spectroscopy," XIth International Conference on Photochemistry, University of Maryland (August 1983).

21. R.W. Field, "Stimulated Emission and Quantum Beat Spectroscopy: The $H_2CO \rightarrow H_2 + CO$ Barrier and Quantum Chaos in the Acetylene $\tilde{X}^1\Sigma_g^+$ State," International Workshop on Primary Photophysical Processes, Herrsching, Germany (October 1983).

22. R.W. Field, "A Time Independent View of Intramolecular Vibrational Redistribution: Coriolis Perturbations in Formaldehyde and Quantum Chaos in Acetylene," International Conference on Radiationless Transitions, Newport Beach, California (January 1984).

23. J.L. Kinsey, "Stimulated Emission and Quantum Beat Spectroscopy," American Physical Society, Los Angeles (March 1983).

24. R.W. Field, same as #22, University of Arizona, Department of Chemistry (November 1983).

25. R.W. Field, same as #22, Northeastern University, Department of Chemistry (November 1983).

26. R.W. Field, same as #22, Syracuse University, Department of Chemistry (February 1984).

27. R.W. Field, "Stimulated Emission Spectroscopy: Structure, Isomerization, and Chaos", University of Pennsylvania, Department of Chemistry (April 1984).

28. R.W. Field, same as #27, MIT Modern Optics and Spectroscopy Series (May 1984).

29. J.L. Kinsey, "Evidence for Quantum Chaos in the Stimulated Emission Pumping Spectrum of Acetylene near 28000 cm^{-1}", Conference on Quantum Chaos, Los Alamos National Lab. (March 1983).

Interactions: Spoken Papers (continued):

30. J.L. Kinsey, "Energy Redistribution in Acetylene?", DOE Contractors' Meeting, Brookhaven National Lab. (May 1983).

31. J.L. Kinsey, "Chemical Dynamics Studied by Emission Spectroscopy of Dissociating Molecules", University of North Carolina (September 1983).

32. J.L. Kinsey, same as #31, University of California (November 1983).

33. J.L. Kinsey, same as #31, Tulane University (November 1983).

34. J.L. Kinsey, same as #31, Texas A&M University (December 1983).

35. J.L. Kinsey, same as #31, Rice University (December 1983).

36. J.L. Kinsey, same as #31, Harvard University (January 1984).

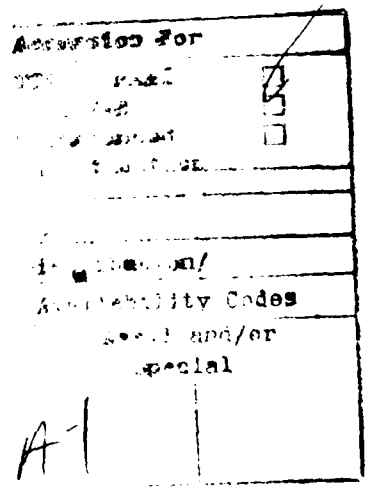
37. J.L. Kinsey, same as #31, Northeastern University (January 1984).

38. J.L. Kinsey, same as #31, University of Rochester (February 1984).

39. J.L. Kinsey, "Stimulated Emission and Quantum Beat Spectroscopy of Formaldehyde and Acetylene", 8th International Symposium on Gas Kinetics, University of Nottingham, England (July 1984).

G. Patents

None.



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